TRANSLATION

(19) European Patent Office

(11) Publication No.: **0 239 036 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application No.: 87104146.3

(51) Int. Cl.[4]: **B29C 45/00,** C08J 5/00 //B29K 67/00, B29K 77/00

(22) Application Date: 20 March 1987

(30) Priority: 22 March 1986 DE 3609805

(43) Publication Date of application: 30 September 1987 Patentblatt 87/40

(84) Designated Contracting States: BE CH DE FR GB IT LI SE

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(54) **Process for Producing Molded Structures from Liquid Crystalline Polymers**

(57) The invention involves a process for producing molded structures having isotropic mechanical properties by injection embossing of liquid crystalline polymers.

Process for Producing Molded Structures from Liquid Crystalline Polymers

The invention involves a process for producing molded structures from liquid crystalline polymers by the injection embossing process.

The thermoplastic processing of thermotropic liquid crystalline polymers yields materials having exceptional properties, in particular, high strength and rigidity. Furthermore, the molding compositions are extensively resistant to organic solvents and also difficultly flammable without the addition of flame protectants.

If the processing of liquid crystalline polymers is attempted by the conventional injection molding process, molded structures having higher anisotropy of mechanical properties are obtained as a result of the orientation of the polymer chains.

Therefore, the invention is based on the problem of producing molded structures from liquid crystalline polymers having largely isotropic mechanical properties.

This problem is solved if the liquid crystalline polymers are processed by the injection embossing process.

Injection embossing is a process technique known for the processing of thermoplastics as described, for example, by I. Wallner, Plastverarbeiter 6, page 229 (1961), H. Dräger and W. Woebecken "Pressen und Spritzpressen" (Compression Molding and Injection Molding), Hanse Verlag, Munich, 1955, and in EP –A-56 702.

Until now, only polymers from an isotropic phase have been processed by the injection embossing process. It is surprising that in processing liquid crystalline polymers having an anisotropic phase of stiff molecular chains, molded structures having isotropic mechanical properties are obtained by injection embossing.

In injection embossing, the thermoplastic melt is injected at a temperature of at least 70° C, preferably 100 to 120° C above the glass temperature of the thermoplastic or at least 20°C, preferably 30 to 40° C above the melting point of the partially crystalline system, in a mold having a movable mold wall, so that the mold is filled only partially, preferably to less than 98 volume percent, in particular between 90 and 97 volume percent.

The form is then closed to complete filling under isobaric conditions and an embossing pressure is applied on the movable mold wall so long until at least the temperature has dropped below the glass temperature of the thermoplastic, preferably to at least 50° C below the glass temperature. With partially crystalline systems, the embossing pressure is adjusted so that a pressure-induced crystallization occurs. Subsequently, the embossing pressure is raised to P_{max} and cooled to $T<T_g$.

The internal volume of the mold decreases from the pressure applied on the mold wall and indeed at least by the amount of the volume contraction of the thermoplastic on cooling. However, in addition, it is advantageous to fill the mold only partially. Then, the process can be managed with essentially lower embossing pressures. The maximum embossing pressure is generally between 300 and 900 bar, in particular, between 400 and 700 bar. The average cooling rate is preferably 10° per minute to 2° per second, in particular, 1° per minute to 4° per second.

Thermotropic liquid crystalline polymers are known. These involve fully or partially aromatic polycondensates, such as polyesters, polyester amides, polyether esters, polyester carbonates, polyester amidimides and similar polymers. The term "fully aromatic" means here that each monomer unit in the polymers has at least one aromatic ring for the structure of the polymer chain. The term "partially aromatic" means that a part of the monomer structures forming the chain is not aromatic, that is, is generally aliphatic (linear or cyclic).

The aforesaid polymer classes contain a series of liquid crystalline polymers suited for the invention, but the listing is in no way exclusive; in addition, not all polymers of the aforesaid polymer classes have a liquid crystalline phase.

The existence of a liquid crystalline phase in the polymer melt in each case and thereby, the suitability of the material for use according to the invention can be detected with the aid of polarization microscopy. The method is described thoroughly in DE-AS 25 20 819. Polymer melts, applied in a layer thickness of ca. 10 μm between glass plates placed between polarizers, show textures that can be classified as mesomorphic phases. A thorough synopsis of the polymers in question is contained in EP-A 1 340, EP-A 129 372, EP-A 131 846 and EP-A 139 303.

The preferred polymers form a liquid crystalline phase below 400° C; those that form a liquid crystalline phase below 330° C are preferred. Particularly preferred are fully aromatic polyesters or fully aromatic polyester amides, in particular, those having high partial crystallinity and a glass temperature above 120° C. The melting points of these liquid crystalline polymers are between 200 and 350° C, preferably between 250 and 300° C. Their inherent viscosity is between 1 and 5.5 dl/g (measured in pentafluorophenol at 60° C, 0.1 weight %), preferably between 1.5 and 3.5 dl/g.

The invention's molded structures have high strength and rigidity in an almost isotropic distribution.

Example 1

A fully aromatic polyester as described in EP-A 139 303, Example 1, is prepared from
25 mole parts hydroquinone
25 mole parts 4,4'-dihydroxybiphenyl
50 mole parts 2,7-dihydroxtnaphthalene
125 mole parts 4-hydroxybenzoic acid
100 mole parts terephthalic acid

The inherent viscosity is 3.5 dl/g, measured in a 0.1 weight % solution in pentafluorophenol at 60° C; the glass temperature is 125° C.

The polyester melt (anisotropic liquid crystalline state) is forwarded with a temperature of 320° C into a temperature-controlled injection embossing mold having a movable half, whereby, to begin the fill process, the mold is opened by an embossing gap that is larger than that required

to offset thermal contraction, so that the mold is filled to 96 volume %. The embossing step is launched after partial filling of the mold cavity.

The embossing pressure is adjusted so that the movement of the mold part follows the contraction caused by the cooling of the melt, whereby continual complete contact of the embossing area with the molding composition is ensured. The maximum embossing pressure used is 600 bar, and the cooling rate is 2° C per second. After cooling to the temperature of 70° C, the part is ejected.

To test the isotropy of the mechanical properties, rectangular plates (belt sprue, sidewise) were made, and test structures prepared from these according to DIN 53 457, whereby the longitudinal axes of the test structures are oriented parallel or perpendicular to the sprue direction. Table 1 reproduces the relation of the E moduli $E_?/E_?$. Values for a plate produced in conventional injection molding are given for comparison.

Table 1

	Composition Temperature	Mold Temperature	$E_?/E_?$*
Injection molding	320° C	80	1.28
Injection embossing	320° C	80	1.07

* ? = Subscripts illegible

Examples 2 to 5

A liquid crystalline polyester of the composition described in Example 1 is processed as in Example 1. The composition temperature and mold temperature are varied.

Example	Composition Temperature	Mold Temperature	$E_?/E_?$*
2	300	80	1.05
3	350	80	1.09
4	320	90	1.05
5	320	100	1.04

* ? = subscripts illegible

Claims

1. Process for producing molded structures from thermoplastic polymers by injection embossing, whereby a thermoplastic melt at a temperature that is at least 70° C above the glass

temperature of the plastic is injected into a mold having a movable mold wall so that it is filled only partially, the mold is then closed and an embossing pressure is applied on the movable mold wall at least so long until the temperature has dropped below the glass temperature of the thermoplastic, characterized in that the thermoplastic is a liquid crystalline polymer.

2. Process according to Claim 1, characterized in that the liquid crystalline thermoplastic is partially crystalline, and the thermoplastic melt is processed at a temperature that is at least 20° C above the melting point T_m so that, at an embossing pressure $P<P_{max}$ and a temperature $T>T_m$ ($P = 1$ bar) a pressure-induced crystallization occurs.

3. Process according to Claim 1, characterized in that the thermoplastic is a fully aromatic polyester or polyester amide.

(Translators' note: The next page in the German document is a duplicate of the first page, except that the A2 with the publication number has been changed to A3 to indicate the publication of the European Search Report, which is translated on the next page here.)

European Patent Office

European Search Report

Application Number
EP 87104146.3

REFERENCES CONSIDERED RELEVANT			
Category	Reference and Relevant Text	Relevant to Claim	Classification of Application (Int.Cl.[4])
Y	DD – A – 122 493 (ENGEL) * Page 2, lines 1-20 * ---	1, 3	B 29 C 45/00 C 08 J 5/00 //B 29 K 67:00 B 29 K 77:00
Y	EP – A1 – 0 053 940 (CELANESE) * Claims; page 5, lines 26-32 * ---	1, 3	
P, Y	DE – A1 – 3 526 727 (CELANESE) * Abstract; page 21, lines 1-5 * ----	1, 3	
			Technical Fields Searched (Int.Cl.[4])
			B 29 C C 08 J C 08 G
This report covers all claims			

Place of Search	Search Completion Date	Examiner
Vienna	9 November 1987	MAYER

Category of Cited References

X: Particularly relevant alone
Y: Particularly relevant combined with another reference in the same category
A: Prior art

O: Non-written disclosure
P: Intervening reference
T: Theory or principle underlying the invention

E: Prior patent reference, but published on or after filing date
D: Cited in application
L: Cited for other reasons

&: Member of same family, equivalent document

Translation: Language Solutions
Philip M. Levin, Sci-Tech Translation Service
3 October 2004